Quiz 5

CH 353 Sumer 2010

Vanden Bout

Name: Key

Carefully read all the problems. The first page has potentially useful information. The last page is for extra writing space.

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $R = 8.314\text{x}10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}$ $R = 8.206\text{x}10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}$

1 atm = 1.01325 bar T/K = T/°C + 273.15 1 atm-L = 101.325 J 1 bar-L = 100 J

$g = 9.8 \text{ m s}^{-2}$ $\Pi = \rho g h$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \qquad \ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Delta T = KX_B \quad K \equiv \frac{RT_b^{*2}}{\Delta_{VAP}H} \qquad \Delta T = K'X_B \quad K' \equiv \frac{RT_m^{*2}}{\Delta_{FUS}H}$$

$$\Pi = \frac{n_B}{V} RT = [B]RT$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_M \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = -S_M$$

$\Delta_R G° = -RT\ln K$

Please sign at the bottom to certify that you have worked on your own.

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: --

Signature Date

1. True/False Circle either T or F for each statement (10 points each)

T F Given that Hg(l) has a higher density (thus smaller molar volume) than Fe(s), the activity of Hg(l) at standard pressure will be very slightly less than that of Fe(s).

T F For the following reaction $\Delta_R G°$ greater than zero.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

T F For the following reaction adding an inert gas such as Ar will decrease the equilibrium constant

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

T F If K > 1, then $|T\Delta_R S^0| > |\Delta_R H^0|$

$-RT \ln K = \Delta H_R^\circ - T\Delta S_R^\circ$

$K > 1$ means lhs is $\ominus$

So $|T\Delta S_R^\circ| > |\Delta H_R^\circ|$ ✓

T F If $\Delta_R S° < 0$, the equilibrium constant for a reaction will always decrease with increasing temperature

$-RT \ln K = \Delta H_R^\circ - T\Delta S_R^\circ$

$R \ln K = -\frac{\Delta H_R^\circ}{T} + \Delta S_R^\circ$

$\ominus$

if ΔH_R° is $\ominus$, then $\uparrow T$ will $\downarrow K$.

if ΔH_R° is $\oplus$, then $\uparrow T$ will $\uparrow K$

2A. (20 points) → heat is a product

The following exothermic reaction is found at equilibrium at a pressure of 10 bar and a temperature of 500K.

heat

$$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g) + q$$

What will happen to the amount of methanol at equilibrium when

The temperature is raised → like adding product	Increase	Decrease	Unchanged
The pressure is raised	Increase	Decrease	Unchanged
An inert gas is added at constant pressure	~~Increase~~	Decrease	Unchanged
An inert gas is added at constant volume	Increase	Decrease	Unchanged

2B. (30 points)

For the reaction

$$2NOCl\ (g) \leftrightarrow 2NO(g) + Cl_2(g)$$

K = 1.6 x 10^{-5} at 35°C.

Given these conditions you have a container that has 2 moles of NOCl, 2 moles of NO, and 1 mole of Cl_2 in a container that has a volume of 2000 L at a temperature of 35°C.
Is the system at equilibrium? If not, which way will the reaction proceed to reach equilibrium (towards the reactants or towards the products)?

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$$K = \frac{(P_{NO}/p^\circ)^2}{(P_{Cl_2}/p^\circ)(P_{NOCl}/p^\circ)^2}, \quad p^\circ = 1\text{ bar}$$

Partial Pressure of:

$$P_{NOCl} = \frac{n_{NOCl}RT}{V}$$

$P_{NOCl} = 0.0256$ bar

$P_{NO} = 0.0256$ bar (+5)

$P_{Cl_2} = 0.0128$ bar

$$1.6\times10^{-5} \overset{?}{=} \frac{(0.0256)^2}{(0.0128)(0.0256)^2}$$

$1.6\times10^{-5} \neq$ ~~78.125~~ $\boxed{\text{NOT at Equilibrium}}$ (+10)

(+5) ↑ This is Q. Since Q > K, reaction will shift towards the $\boxed{\text{reactants.}}$ (+15)

0.0128

3. (25 Points)

For the following reaction

$A(s) \rightarrow 2B(g) + C(g)$

You start with 1 moles of solid a in an evacuated chamber that is held at a constant temperature of 500K. The system evolves to equilibrium at which point you find the partial pressure of gas C is 5 Torr. What is $\Delta_R G°$ for this reaction at 500K.

(+5) $K = \frac{P_C}{P^\ominus}\left(\frac{P_B}{P^\ominus}\right)^2$, $P^\ominus = 1\text{ bar}$, so $K = P_C P_B^2$ $\quad P_B = 2P_C$ (+5) (from rxn Stochiometry)

$K = P_C(2P_C)^2 = 4P_C^3$

$K = 4\left(\frac{5}{750}\right)^3 = \cancel{500}$ (+5) 1.185×10^{-6}

$\Delta_R G° = -RT\ln K = -(8.3145)(500\text{ K})\ln(\cancel{500}\ 1.185\times10^{-6}) = \boxed{-25.8\text{ kJ/mol}}$ $\boxed{5.67\times10^4\text{ J/mol}}$ (+10)

4. (25 Points) Below is a plot of lnK vs 1/T for a reaction. Use the tangent line to extract the change in enthlapy and entropy for the recation at 250 K. Note: as the plot is not a straight line one cannot assume the enthalpy and entropy are indepent of temperature.

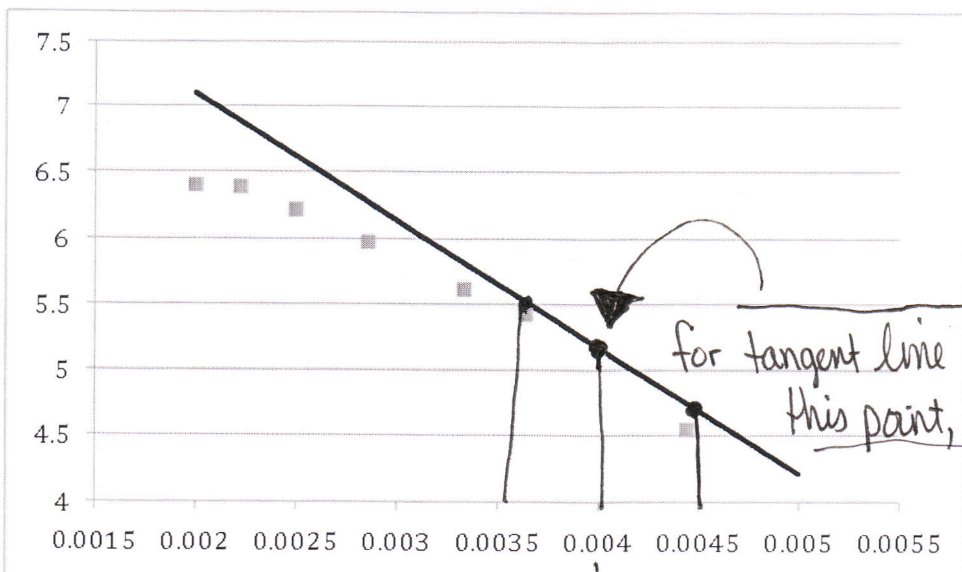
$\frac{1}{250\text{K}} = 0.004$

Slope $= -\Delta H_R°/R$

Int $= \Delta S_R°/R$

$m = \frac{(4.75)-(5.5)}{(0.0045)-(0.0035)\ 1/\text{K}}$

$m = -750\text{ K}$ (+5)



for tangent line at this point, find $\Delta H_R°$, $\Delta S_R°$

$5.5 = -750(.0035) + b$

$b = 8.125$ (+5)

$\Delta H_R° = -\text{slope}\cdot R$

$\Delta H_R° = -(-750)(8.3145) = \boxed{6236\ \frac{\text{J}}{\text{mol}}}$ $1/250\text{K}$ (+5)

$\Delta S_R° = \text{int}\cdot R = 8.125(8.3145) = \boxed{67.6\text{ J/K·mol}}$ (+5)

Equation of line:

$\ln K = -750\frac{1}{T} + 8.125$

(+5)

4. (50 points)

Consider the following reaction

$$2A(s)+B(g)\rightarrow 2C(g)$$

You initially start with 4 moles of solid A and 1 mole of gas B in a container at a constant temperature of 400K and a pressure of 2 bar. For this reaction $\Delta_R G° = 5$ kJ mol^{-1}. You let the system come to equilibrium and measure that 4100 J of heat is absorbed by the system to maintain a constant temperature. Use this information to determine the partial pressure of the gas C in equilibrium at the higher temperature of 600K and a pressure of 2 bar.

	$2A(s)$ +	$B(g)$ $\rightarrow$	$2C(g)$
r:	$2A_{(s)}$ +	$B_{(g)}$ $\rightarrow$	$2C_{(g)}$
i:	4 moles	1 mole	0 mole
c:	-2ξ	$-\xi$	$+2\xi$
e:	$4-2\xi$	$1-\xi$	2ξ
MF:		$\frac{1-\xi}{1+\xi}$	$\frac{2\xi}{1+\xi}$
P_x:		$\frac{1-\xi}{1+\xi}P_{Tot}$	$\frac{2\xi}{1+\xi}P_{Tot}$

total gas moles: $1-\xi+2\xi = \underline{1+\xi}$

$K = e^{-\Delta G°_R/RT} = e^{-5000/8.314(400)}$

$K = 0.2224$

$K = 0.2224 = \frac{(P_C/p^{\circ})^2}{(P_B/p^{\circ})}$, $p^{\circ} = 1$ bar, so $0.2224 = \frac{\left(\frac{2\xi}{1+\xi}P_{Tot}\right)^2}{\left(\frac{1-\xi}{1+\xi}P_{Tot}\right)}$, $P_{Tot} = 2$ bar

$$0.2224 = \frac{\left(\frac{4\xi}{1+\xi}\right)^2}{\left(\frac{2-2\xi}{1+\xi}\right)} = \frac{16\xi^2}{(2-2\xi)(1+\xi)} = \frac{16\xi^2}{2-2\xi+2\xi-2\xi^2} = \frac{16\xi^2}{2-2\xi^2}$$

$$0.4448 - 0.4448\xi^2 = 16\xi^2 \Rightarrow 0.4448 = 16.4448\xi^2 \Rightarrow \xi = 0.1645$$

$$q = \xi\cdot\Delta H_R° \Rightarrow 4100\text{ J} = 0.1645\,\Delta H_R° \Rightarrow \Delta H_R° = 24924\text{ J/mol}$$

Find new K: $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_R°}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow \ln\left(\frac{K_2}{0.2224}\right) = \frac{24924}{8.3145}\left(\frac{1}{400}-\frac{1}{600}\right)$

K @ 600K = 2.70

Now we must redo rice table.

$$r: \quad 2A_{(s)} + B_{(g)} \longrightarrow 2C_{(g)}$$

$$i: \quad 1-\xi \qquad 2\xi$$

where ξ was $= 0.1645$

$$0.8355 \qquad 0.329$$

$$Q = P_C^2 / P_B = \frac{.565^2}{1.435} = 0.2224$$

$$C: \quad -\xi \qquad +2\xi$$

$Q < K$ so shift to products.

$$e: \quad 0.8355-\xi \qquad 0.329+2\xi$$

$$MF: \quad \frac{0.8355-\xi}{1.1645+\xi} \qquad \frac{0.329+2\xi}{1.1645+\xi}$$

$$P_X: \quad \frac{0.8355-\xi}{1.1645+\xi} P_{Tot} \qquad \frac{0.329+2\xi}{1.1645+\xi} P_{Tot}$$

$$K = 2.70 = \frac{\left(\frac{0.329+2\xi}{1.1645+\xi}\right)^2 P_{Tot}^2}{\left(\frac{0.8355-\xi}{1.1645+\xi}\right) \cancel{P_{Tot}}}$$

$$1.35 = \frac{(0.329+2\xi)^2}{(1.1645+\xi)(0.8355-\xi)} = \frac{(0.10824+1.316\xi+4\xi^2)}{(0.9729-0.329\xi-\xi^2)}$$

$$1.3134 - 0.4442\xi - 1.35\xi^2 = 0.10824 + 1.316\xi + 4\xi^2$$

$$5.35\xi^2 + 1.7602\xi - 1.2052 = 0$$

$$\xi^2 + 0.3189\xi - 0.2253 = 0$$

$$\frac{-0.3189 \pm \sqrt{0.3189^2 - 4(1)(-0.2253)}}{2} = \cancel{0.3413} \quad 0.3378$$

$$P_C = \cancel{1.344} \; 1.337 \text{ bar}$$

$$P_B = \cancel{0.6564} \; 0.6626 \text{ bar}$$